Message

From: Sara Valsecchi [valsecchi@irsa.cnr.it]
Sent: 11/19/2019 6:17:14 PM
To: Strynar, Mark [Strynar.Mark@epa.gov]
CC: McCord, James [mccord.james@epa.gov]; Stefano Polesello [polesello@irsa.cnr.it]
Subject: Re: SETAC Dublin
Attachments: PFECA_extended_abstract.doc; Abstract short PFECA SETAC 2020final.docx

Yes,

I can read the files.

Sample	Coordinate geografiche N (°)	Coordinate geografiche E (°)
BO-M	44.88512	8.63529
BO-V	44.92777	8.66924

Sonia agrees to be on board.

Attached you can find the draft of the extended abstract. I could not confirm you the final version of the short one because I am waiting for the people of the Veneto Region (They do not know if they have the authorization for participating). However I also attached it (in case you can submit to your head office even if the authors are not confirmed)

Ciao

Sara

On 19/11/2019 18:18, Strynar, Mark wrote:

Sara,

Here they are as CDX files. Let me know if you can open these. I will need to go look for the IS you added to the water samples. This gives me some clarity.

Do you have GPS coordinates for the sampling locations on the Bormida river? I did not see that in the Excel file you sent.

Mark

From: Sara Valsecchi <valsecchi@irsa.cnr.it>
Sent: Thursday, November 14, 2019 9:17 AM
To: Strynar, Mark <Strynar.Mark@epa.gov>
Cc: McCord, James <mccord.james@epa.gov>; Stefano Polesello <polesello@irsa.cnr.it>
Subject: Re: SETAC Dublin

Thank for the files but I cannot used them because I haven't Chemsketch Drawing.

Can you save them as .skc or as CS ChemDraw (*.cdx) ?

Thank you

Sara

On 12/11/2019 19:09, Strynar, Mark wrote:

I meant to send these files along that are Chemsketch files for the cC6O4 data and the Cl-PFECAs we see.

Mark

From: Sara Valsecchi <valsecchi@irsa.cnr.it>
Sent: Wednesday, November 06, 2019 6:28 AM
To: Strynar, Mark <Strynar.Mark@epa.gov>
Cc: McCord, James <mccord.james@epa.gov>; Stefano Polesello <polesello@irsa.cnr.it>
Subject: Re: SETAC Dublin

Great!

Actually in-source fragmentation can be a problem.
Did you try to look for cC6O4 in the Bormida 2013 that you analysed? I found traces of cC6O4 in Tanaro 2012 (that receives Bormida) so there are some chances that cC6O4 was also present in Bormida 2013.

However I will send you a technical mixture with cC6O4 (please send me the right mail address). I don't know if in the mixture other PFASs are present. I'd like to know.
You have to wait for Bormida, Po Rivers extracts because it is raining a lot and the flows have to be lower for sampling. However I will do it

May you send me what you have already presented at ACS in Orlando so I can have ideas for the abstract. If you have already something in mind let me know.
Ciao
Sara

On 04/11/2019 17:19, Strynar, Mark wrote:

Hi Sara,

Glad to submit an abstract with you. I have looked for the cC6O4 in our water samples from NJ but did not see any. That is unless it does something weird in our source. I looked for the M-H, and the H+ and Na+ gas phase dimers. We essentially have quite a bit of the Solvay n,m compounds in water, soil and plants. We are getting ready to submit a pub soon. I have presented some of this info at ACS in Orlando, FL in the spring so I am glad to show more. I would love some of the water or an extract with the cC6O4 in it (or some additional Bormida or Po river samples) so we can give it a look with our Orbitrap also. I think my colleague James McCord would like to be involved.

Mark

From: Sara Valsecchi <valsecchi@irsa.cnr.it>
Sent: Monday, November 04, 2019 6:34 AM
To: Strynar, Mark <Strynar.Mark@epa.gov>
Subject: SETAC Dublin

Dear Mark,
Abstract submission deadline to the next SETAC European Annual Meeting is November 27. I would like to attend and I am wondering if we (together) can submit a abstract (for a Poster) about the new PFASs (cC6O4 and Solvay n,m) that Solvay is discharging. It does not matter if we cannot quantify the concentration but we can just to stress that two factories of the same company are discharging the same compounds. If you cannot spread what Solvay in NJ is discharging , for internal obstacles, we can just report the Italian site. However I would like that you are involved in the poster.
Of course all the people involved will be co-authors.
Let me know what you think
Ciao from Italy
Sara

On 19/10/2019 22:11, Sara Valsecchi wrote:

Dear Mark,

Yes, the CAS number of compound I call cC6O4 is 1190931-41-9.

European Food Safety Authority (EFSA) released a Scientific Opinion on the safety assessment of the ammonium salt, CAS No 1190931-27-1 for use in food contact materials (attached). The European Chemical Agency (ECHA) has a Registration Dossier on it (Attached - Miteni and Solvay Solexis in Italy are the two Active Registrant Suppliers for Europe)

It took me sometime to understand the differences between your and my results and found out my mistakes. It was some years ago and I had to reconstruct the story .

Some points to be considered:

- Solvay discharges into the Bormida River; few km downstream the Solvay's discharge the Bormida River flows into the Tanaro River; the Tanaro River flows into the Po River (the longest River in Italy but short if compared to North American ones). About 250 km after the confluence of the Tanaro River the water of the Po River is used to produce drinking water.

- The HRMS analyses that I have were not carried out with the purpose of Suspect Screening of new PFAS. The samples were analysed for other aims and I stored the LC-MS HRMS FullScan raw file for future retrospective investigations. I have an analysis of Tanaro River in 2012 carried out by on-line SPE injection (5 mL) (in Norman Bull we reported Bormida but it is wrong). Moreover I have an analysis of Bormida River 2017 carried out by direct injection (100 uL). The

sensibility of my analyses could be not high enough.

- I made a mistake in calculation the possible combination of the PFECAs of Solvay Wang et al., 2013 paper (I forgot the combinations with n=0)

PFECA compounds

Taking into consideration these remarks and looking for the PFECA structures that you detected in Bormida River 2013:

-Solvay 1,0 + cC6O4 were detected in Tanaro River 2012 (Bormida dilutes in the Tanaro at least 5 times).

-Solvay 1,0+Solvay 0,1+cC6O4 were detected in Bormida River 2017, the Solvay 1,0 is the dominant compound (see attached .doc)

Since in Bormida River 2013 you found that Solvay 1,0 was the dominant compound I suppose that the composition of the PFECA mixture is constant. I did not found all the PFECA structures because the Tanaro 2012 is too diluted and the Bormida 2017 was a direct injection analyses whereas you analysed more concentrated extracts.
(be careful: the n and m in your figure of Bormida River 2013 are inverted comparing to the formula you attached to the email. Moreover your reported the 0,2 combination twice).

If you are interested to go on in the investigation (I am) I might sample the Bormida River, extract the samples and send you the cartridges for analysis. So we will have a Bormida 2019 analyses. Also if you have the Mass Spectra of the different compounds you could send me the precursors and the main fragments. I already have to analysed cC6O4 in Bormida River and I might look for the PFECA compounds (by LC-MS triple quadrupole).

Moreover (I am not sure, I have to check) I have Bormida River Samples (kept frozen) that were collected in other years (2014, 2015...). I (or you) could analysed them for trend analyses.

cC6O4 Cas n.1190931-41-9

Regarding cC6O4, it was detected by the Local Environmental Agency in the drinking water produced by Po River (about 250 km far from Tanaro River confluence; the dilution factor between Tanaro and Po River is about 30-40 and this roughly is the ratio between PFOA concentration in Po River and in in Tanaro River). They use a LC-MS triple quadrupole (precursor is 338.9557 and fragments are 178.9773 and 112.9856). They were looking for it because they have a technical mixture of this compound. The concentration of it in drinking water was evaluate around 50 ng/L (we can infer that the concentration in Bormida might be more than 5 µg/L). Now the certified standard is ready and we are in charge to monitoring the Bormida River and the Po River.

I suppose that also the PFECAs may be present in the drinking water (at least the dominant one: Solvay 1,0). I can try to have drinking water samples or, with the precursors and the fragments, I can ask to Local Agency to look for the PFECAs.

Do not mind for a quick answer. We are all so busy but I am very pleased to chat on this and to collaborate. Soon

Ciao
Sara

On 15/10/2019 16:30, Strynar, Mark wrote:

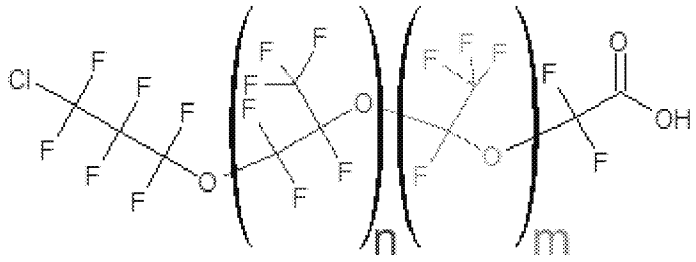
Sara,

Sorry for the slow reply. There is a lot here and a lot to share with you as well.

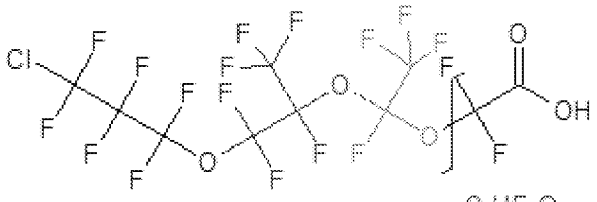
I need to dig through what you sent however I can confirm a few things. We have found all of these Cl-PFPECAs in the NJ and Bormida river samples (see attached docs). It was not just the C8HF14O4Cl compound, PFOA was also quite abundant. However the ratios of the analytes found are different. In the NJ water most of the signal (97%) was from one analyte. As you can see in your samples there was still C8HF14O4Cl, but several others and not in low abundance.

In the Wang et al., 2013 paper we have found many of the Markush structures for the Cl containing PFECAs

Solvay
CAS 329238-24-6



Solvay 1,1

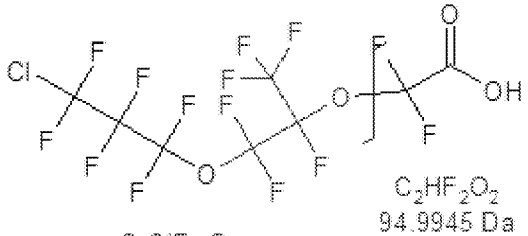


$C_8ClF_{16}O_3$
482.928 Da

$C_2HF_2O_2$
94.9945 Da

Monoisotopic Mass: 577.922508 Da

Solvay 1,0

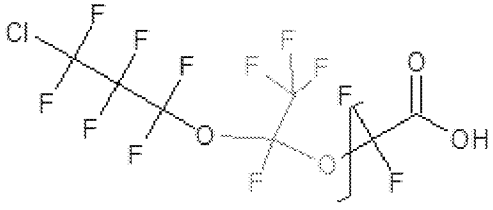


$C_6ClF_{12}O_2$
366.9395 Da

$C_2HF_2O_2$
94.9945 Da

Monoisotopic Mass: 461.933981 Da

Solvay 0,1

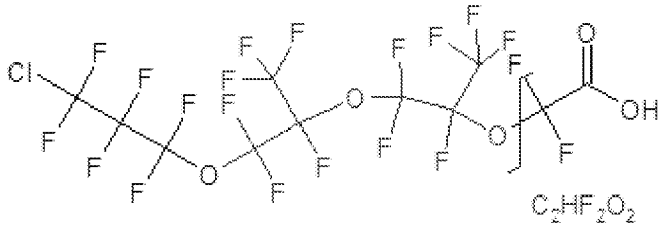


$C_5ClF_{10}O_2$
316.9427 Da

$C_2HF_2O_2$
94.9945 Da

Monoisotopic Mass: 411.937175 Da

Solvay 2,0

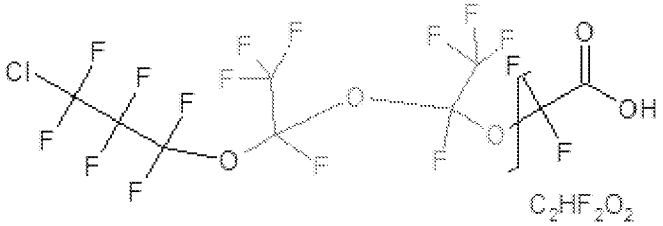


$C_8ClF_{16}O_3$
532.9249 Da

$C_2HF_2O_2$
94.9945 Da

Monoisotopic Mass: 627.919315 Da

Solvay 0,2



$C_7ClF_{14}O_3$
432.9312 Da

$C_2HF_2O_2$
94.9945 Da

Monoisotopic Mass: 527.925702 Da

I believe we may have also found the cC6O4 as you call it. Can you confirm this is CAS 1190931-41-9?

We have a lot of experience with gleaning from Orbitrap and Agilent QTOF data. We would be glad to work with you on this front.

Mark

From: Sara Valsecchi <valsecchi@irsa.cnr.it>
Sent: Thursday, October 03, 2019 10:39 AM
To: Strynar, Mark <Strynar.Mark@epa.gov>; Dagnino, Sonia <sonia.dagnino@imperial.ac.uk>
Cc: Lindstrom, Andrew <Lindstrom.Andrew@epa.gov>; Stefano Polesello <polesello@irsa.cnr.it>
Subject: Re: Samples from Bormida analyzed at the EPA

Dear Mark,
thank you very much for contacting me and keep me informed.
Probably you are not aware but I attended last August the SETAC PFAS meeting in Durham. I was involved in the WG-Ecotoxicology. Compliments for your interesting presentation.

Just to give you an idea of a picture of the contaminated areas in Italy I attached the papers that we published in Chemosphere and STOTEN
We have a Fluoropolymer plant (Solvay Solexis) that discharges into the river Bormida and we had a Fluorochemical plant (Miteni) located in the Veneto Region (but it closed few weeks ago for insolvency). The aquifer of the Veneto Region is heavily impacted by PFOA and short chain PFCA. We did not publish in detail the Veneto Region contamination because the local authorities did not want to scare too much the people that drank for long time the contaminated drinking water. Monitoring of PFAS blood levels and population health are on going. Moreover local authorities are carrying out an intensive monitoring of the drinking water and food stuff. We are collaborating with them regarding the contamination of vegetable irrigated by contaminated waters. Attached you can find a WHO report on this hot spot we discovered on 2013.

I am very happy that you analysed and identified new PFAS in Bormida river. In fact we carried out some researches on new PFAS substances but we have not an LC-HRMS and so we could just carry out some analyses in few samples in the framework of collaborations (as it happened with Sonia).
In the Bormida river we looked for the compounds that Solvay should have used to replace PFOA into the PTFE production (river was collected in 2015). The exact masses of these compounds corresponded to a elemental formula of C8HF14O4Cl (newsletter_norman_4_11032015.pdf). I do not have MS/MS mass spectra of this peak. Is this the same exact mass that you find in the the extract of river sampled in 2013?

Recently (before summer) another compound (cC6O4) has been identified in the water of river Po (that receives the River Bormida's waters) by Veneto Region. cC6O4 was produced by Miteni and sold to Solvay to replace PFOA in Solvay PTFE production. Attached you can find some documents regarding this compound.
Soon we'll have the cC6O4 pure standard (it is produced by chemical synthesis) and we will be able to confirm our suspects.

Furthermore I identified, by retrospective analysis, both C8HF14O4Cl and cC6O4 in the river water collected in

2015.

Moreover we investigated the presence of perfluorinated replacement chemicals by applying suspect High-Resolution Mass Spectrometry (HRMS) analysis on liquid wastes, analysed before disposal in landfill or incineration plants located in Northern Italy has been carried out in 2017 (attached the draft of the incoming Norman Bull and a SETAC poster).

Even if we have not the LC-HRMS we are exploring the implementation of the non-target screening. We are collaborating with labs equipped with orbitrap and we are training on the non-target screening approaches using Thermo Compound Discover software.

We are definitively interested to keep in touch with you and also to collaborate for articles, if you think that this can be of interesting for you.

For example I might screen my HRMS files with your PFAS database or I might send to you my raw files (they are acquired by orbitrap and I know you have an TOF but they should be easily converted). Moreover we might collect samples of industrial contaminated waters (e.g. Bormida river, contaminated aquifers, rivers receiving tanneries or textile discharges...) and send you the extraction cartridges (SPE).
Let me know
Best

Sara

On 02/10/2019 21:25, Strynar, Mark wrote:

Sara,

I was also recently forwarded these two documents. It appears you or someone else already identified at least one of theses chemicals in the Bormida River (Norman Bulletin page 6 figure 2b PFEPE). Still glad to chat and exchange knowledge.

Mark

From: Dagnino, Sonia <sonia.dagnino@imperial.ac.uk>
Sent: Wednesday, October 02, 2019 5:24 AM
To: valsecchi@irsa.cnr.it
Cc: Strynar, Mark <Strynar.Mark@epa.gov>
Subject: Samples from Bormida analyzed at the EPA

Dear Sara,

I hope you are doing well.

I don't know if you remember me, we met at the SETAC Glasgow in 2013, at the time I was a post-doctoral fellow at the US EPA in North Carolina working with Dr. Mark Strynar on the analysis of novel PFASs in biological and environmental samples. We discussed about the analysis of PFSAs in the Bormida river, and you sent me a couple of cartridges from your sampling campaign to extract and run on our LC-TOF.

Recently, Mark has identified some novel perfluorinated compounds in effluents from a Solvay plant in New Jersey. He had the idea to retrospectively mine the data that I had aquired on your samples, and he identified the same novel compound present in one of your samples from Bormida.

I am therefore writing to put you both in contact as I think it is a valuable information that needs to be pursued.

Best Regards,

Sonia Dagnino

Research Fellow

Imperial College London, School of Public Health
MRC Centre for Environment and Health

London, W21PG

sonia.dagnino@ic.ac.uk

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